

## DECLARATION

I, Yasuco ISHIDA, SHIGA INTERNATIONAL PATENT OFFICE,  
1-9-2 Marunouchi, Chiyoda-ku, Tokyo, Japan, understand both English and  
Japanese, am the translator of the English document attached, and do  
hereby declare and state that the attached English document contains an  
accurate translation of Japanese Patent Application No. 2004-041335 and  
that all statements made herein are true to the best of my knowledge.

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[Document Name] Claims

[Claim 1]

A hybrid wherein a polymer crystal having a  
straight-chain polyethyleneimine skeleton is covered with a  
5 silica.

[Claim 2]

The hybrid according to claim 1, wherein said  
polymer having the straight-chain polyethyleneimine skeleton  
is a polymer in the form of a line.

10 [Claim 3]

The hybrid according to claim 1, wherein said  
polymer having the straight-chain polyethyleneimine skeleton  
is a polymer in the form of a star.

[Claim 4]

15 The hybrid according to claim 1, wherein said  
polymer having the straight-chain polyethyleneimine skeleton  
is a polymer in the form of a comb.

[Claim 5]

The hybrid according to any one of claims 1 to 4,  
20 wherein said polymer having the straight-chain  
polyethyleneimine skeleton is composed of a block copolymer  
between a straight-chain polyethyleneimine block and other  
polymer blocks.

[Claim 6]

25 The hybrid according to any one of claims 1 to 5,  
wherein a proportion of the polyethyleneimine skeleton in  
said polymer having the straight-chain polyethyleneimine  
skeleton is not less than 40% by mol.

[Claim 7]

30 The hybrid according to any one of claims 1 to 6,  
wherein said polymer crystal is a polymer crystal in  
the form of a filament having a diameter of nanometer  
order.

[Claim 8]

35 The hybrid according to any one of claims 1 to 6,  
wherein said polymer crystal has a three-dimensional

form in which filament polymer crystals of nanometer order are aggregated by means of a physical bond.

[Claim 9]

The hybrid according to any one of claims 1 to 6,  
5 wherein said polymer crystal has a three-dimensional network structure in which crystals having a three-dimensional form in which filament polymer crystals of nanometer order are aggregated are further aggregated by means of a physical bond.

10 [Claim 10]

The hybrid according to any one of claims 7 to 9, wherein a diameter of said filament polymer crystal ranges from 5 to 30 nm.

[Claim 11]

15 The hybrid according to claim 10, wherein said three-dimensional network structure is formed by crosslinking with a crosslinker by means of a chemical bond.

[Claim 12]

20 The hybrid according to any one of claims 1 to 11, wherein a fluorescent substance is contained in said polymer crystal.

[Claim 13]

25 The hybrid according to any one of claims 1 to 12, wherein an amount of said silica in said hybrid is in the range of from 30% by weight to 90% by weight.

[Claim 14]

A method for producing a hybrid between a polymer having a straight-chain polyethyleneimine skeleton and a  
30 silica, comprising the steps of: mixing a polymer having a straight-chain polyethyleneimine skeleton and water or a mixed solvent of water and a hydrophilic organic solvent; heating the mixture to dissolve said polymer having the straight-chain polyethyleneimine skeleton; subsequently  
35 reducing temperature of said solution to form a polymer crystal having a straight-chain polyethyleneimine skeleton

to obtain a hydrogel including water or a mixed solvent of water and the hydrophilic solvent in a three-dimensional network structure composed of said polymer crystals; and subsequently adding an alkoxysilane to said hydrogel.

5           [Claim 15]

The method for producing a hybrid according to claim 14, wherein said alkoxysilane is at least one type selected from the group consisting of tetraalkoxysilanes and trialkoxyalkylsilanes.

10           [Claim 16]

The method for producing a hybrid according to claim 14, wherein said alkoxysilane is a mixture of at least two types selected from the group consisting of tetraalkoxysilanes and trialkoxyalkylsilanes.

15

[Document Name] Specification

[Title of the Invention] Hybrid of polymer crystal and silica and method for producing the same

[Field of technology]

5 [0001]

The present invention relates to an organic-inorganic hybrid in which a polymer crystal of a polymer having a straight-chain polyethyleneimine skeleton is covered with a silica. More particularly, the present invention relates to  
10 a hybrid of a polymer crystal and a silica in which a silica gel is formed on the surface of the aforementioned polymer crystal, and which has a coating layer of a silica in which the form of the polymer crystal is copied.

[Background art]

15 [0002]

Silicon is present on the earth as a second-rich element while the first-rich element is oxygen. Quartz, crystal, opal, mica, asbestos and the like in nature are well-known oxides of silicon. The production of silica  
20 materials having a regular space structure or pattern structure is the major task in the field of material science. Technological development relating thereto has made great progress.

[0003]

25 As a method for expressing a certain type of structure in a silica material, a method in which a molecular aggregate is used as a template and a silica is fixed around the aforementioned aggregate has been widely used in this field. As the aforementioned template, a surfactant (see  
30 Non-Patent Document 1), a block polymer (see Non-Patent Document 2), viruses, bacteria (see Non-Patent Document 3) and the like are used. A silica having nano-cavities synthesized by using them as a template, such as MCM-41 (mesoporous) series can be applied to catalysts, electronic  
35 materials, nano-filters, biotechnology and the like. With respect to the aforementioned materials, studies for

specifically controlling a structure have been performed, and size of cavities, arrangement thereof, cavity control in a spherical silica and the like have been studied.

[0004]

5           On the other hand, concurrently with the  
aforementioned control of nano-cavities, a technology in  
which the form of a silica is controlled from a nano scale  
to a micron scale, and furthermore to a macro scale has  
attracted attention. In a sense, this is enlightened by a  
10   biosilica in the ecological system (see Non-Patent Document  
4). As an example of natural biosilicas, algae may be  
mentioned. In algae, the body thereof is composed of a  
silica, and a complicated and precise form and pattern is  
formed thereon. For the formulation of the silica, proteins  
15   or polypeptides are involved (see Non-Patent Document 5).  
They act as a catalyst for a silica-fixing reaction or  
provide scaffolds of silica form growth. In the formation  
of the aforementioned biological-system biosilica, an  
indispensable chemical structure is a polyamine. The  
20   polyamines act by incorporating into the peptide structure  
or inimitably act together with polypeptides as a polyamine  
having a specified molecular weight (see Non-Patent Document  
6).

[0005]

25           As described above, it has been widely known in recent  
several years that a silica source such as silicic acid,  
sodium silicate or an alkoxysilane can be fixed as a silica  
gel at room temperature in the presence of a polyamine.  
However, they can be carried out by commonly dissolving a  
30   polyamine in water and carrying out a sol-gel reaction of  
the silica source in the aqueous solution. For this reason,  
even if it is possible to form a silica gel, the form of the  
silica gel cannot be controlled, and it is difficult to  
obtain a silica gel having a regular structure.

35           [0006]

[Non-Patent Document 1] C. T. Kresge et al., Nature,

(1992), 359, p. 710

[Non-Patent Document 2] A. Monnier et al., Science,  
(1993), 261, p. 1299

[Non-Patent Document 3] S. A. Davis et al., Nature,  
5 (1997), 385, p. 420

[Non-Patent Document 4] W. E. G. Muller Ed., Silicon  
Biom mineralization: Biology-Biotechnology-Molecular Biology-  
Biotechnology, (2003), Springer

[Non-Patent Document 5] N. Kroger et al., Science,  
10 (1999), 286, p. 1129

[Non-Patent Document 6] N. Kroger et al., Proc. Natl.  
Acad. Sci. USA. (2000), 97, p. 14133

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

15 [0007]

An objective to be achieved by the present invention  
is to provide a hybrid of a polymer crystal of which the  
form is controlled to various forms and a silica, and  
provide a simple method for producing the hybrid of the  
20 polymer crystal and the silica.

[Means for Solving the Problems]

[0008]

In order to obtain a silica in the form of a specified  
form from a sol-gel reaction in water, it is believed that  
25 three important conditions are indispensable. Namely, they  
are (1) a template for deriving a form, (2) a scaffold  
for concentrating a silica source, and (3) a catalyst  
for polymerizing the silica source.

[0009]

30 In the present invention, in order to satisfy the  
aforementioned conditions, a polymer having a  
straight-chain polyethyleneimine skeleton is employed.  
The straight-chain polyethyleneimine is soluble in  
water, but is present as a crystal at room temperature,  
35 and the crystal acts as a template. In addition, on  
the surface of the aforementioned crystal, there are



many free polyethyleneimine chains which are, unavavoidably, not involved in crystallization. These free chains are in the condition of drooping down on the surface of the crystal. These chains are  
5 scaffolds for attracting a silica source, and act as a catalyst for polymerizing the silica source at the same time.

[0010]

Thereby, a sol-gel reaction proceeds on the  
10 surface of the polymer crystal having a straight-chain polyethyleneimine skeleton, and a hybrid of a silica and a polymer crystal of which the surface is covered with the silica of the present invention is formed. In addition, the form of the polymer crystal in the  
15 present invention is copied to the silica. For this reason, the hybrids of the present invention have various complicated forms.

[0011]

In addition, the polymer crystal having a  
20 straight-chain polyethyleneimine skeleton provides a hydrogel of which the form can be easily controlled in the presence of water. For this reason, after the aforementioned hydrogel is formed into a desirable form, and subsequently, the polymer crystals in the  
25 hydrogel are mutually crosslinked by means of a chemical bond with a compound having two or more functional groups, by carrying out a sol-gel reaction, a composite of the hybrid of the silica and the polymer crystal in which the individual crystal form  
30 is incorporated therein can be obtained in a large aggregate of a silica gel.

[0012]

Namely, the present invention provides a hybrid in which a polymer crystal having a straight-chain  
35 polyethyleneimine skeleton is covered with a silica, and a composite of the aforementioned hybrid.

[0013]

In addition, the present invention provides a method for producing a hybrid between a polymer having a straight-chain polyethyleneimine skeleton and a silica, comprising  
5 the steps of: mixing a polymer having a straight-chain polyethyleneimine skeleton and water or a mixed solvent of water and a hydrophilic organic solvent; heating the mixture to dissolve said polymer having the straight-chain polyethyleneimine skeleton; subsequently reducing  
10 temperature of said solution to form a polymer crystal having a straight-chain polyethyleneimine skeleton to obtain a hydrogel including water or a mixed solvent of water and the hydrophilic solvent in a three-dimensional network structure composed of said polymer crystals; and  
15 subsequently adding an alkoxysilane to said hydrogel.

[Effects of the Invention]

[0014]

According to the hybrid between the polymer crystal and the silica of the present invention, by the sol-gel  
20 reaction of a silica source which proceeds only on the surface of filament polymer crystal of nanometer order, the silica having a specified thickness can cover the aforementioned filament polymer crystal of nanometer order. In addition, the aforementioned filament polymer crystals of  
25 nanometer order can form various three-dimensional forms of micrometer order by means of various space arrangements or aggregations caused by the polymer structures forming the filament polymer crystals of nanometer order. In addition, the aforementioned three-dimensional form can form a three-  
30 dimensional network structure. For this reason, controlling macro forms of millimeter order or greater can be carried out. The aforementioned various forms can be fixed by the coating silica layers. For this reason, the hybrid between the polymer crystal and the silica of the present invention  
35 can easily form a complicated structure.

[0015]

In addition, in the hybrid between the polymer crystal and the silica of the present invention, polymer crystals in a complicated form can be mutually crosslinked by means of a chemical bond. At that time, an aqueous dispersion or an aqueous solution in which the polymer crystals are dispersed or a hydrogel containing the polymer crystals are formed into a desirable form, and fixing between the polymer crystals is performed by crosslinking to obtain an aggregate in a macro form. Subsequently, a sol-gel reaction of a silica source is carried out. Thereby, a composite in a macro form of the hybrids covered with the silica can be easily produced. At that time, in the hybrids in a macro form, hybrids having a three-dimensional form of micrometer order are present. In addition, in the hybrids having the three-dimensional form of micrometer order, filament hybrids of nanometer order are present. Therefore, in accordance with the present invention, hybrids between the polymer crystals and the silica having a form dimension of nanometer order, micrometer order, and macro size of millimeter order or greater can be easily produced.

[0016]

In addition, when the hybrid between the polymer crystals and the silica of the present invention is formed, a functional substance such as a fluorescent substance can be contained in the crystals, and thereby, the function derived from the contained functional substance can be exhibited.

[0017]

In addition, the polymer crystals having the straight-chain polyethyleneimine skeleton in the hybrid between the polymer crystals and the silica can be widely utilized in industrial fields, and use thereof in various fields such as the biological field, developments in high-tech materials such as nano materials, examples of which include conductive materials, metal nanofibers, metal oxide nanofibers, polymer-metal complexes in nanospace, biopolymer carriers,

antibacterial agents, biocides, antiviral agents, cosmetics and the like, has been attempted. For this reason, the hybrids of the present invention can be applied to the aforementioned fields.

5 [0018]

In addition, the polymer crystals in the hybrid between the polymer crystals and the silica of the present invention can be easily removed by sintering. For this reason, the present invention can also be applied to  
10 production of a silica nanotube containing a tubular space, and can also be applied to the usage of catalysts, biomaterials, nanofilters and the like.

[Best Modes for Carrying Out the Invention]

[0019]

15 The hybrid of the present invention is formed by covering a polymer crystal having a straight-chain polyethyleneimine skeleton with a silica (silicon oxide).

[0020]

Polymer Having a Straight-chain Polyethyleneimine  
20 Skeleton

The straight-chain polyethyleneimine skeleton referred in the present invention means a polymer skeleton having an ethyleneimine unit of a secondary amine as a main structural unit. In the aforementioned skeleton, structural units  
25 other than the ethyleneimine unit may be present, but it is preferable that the polymer chain in a specified chain length consist of a continuous ethyleneimine unit in order to form a polymer crystal. The length of the aforementioned straight-chain polyethyleneimine skeleton is not  
30 particularly limited as long as the polymer having the aforementioned skeleton can form a crystal. In order to suitably form a polymer crystal, the number of the repeating units of the ethyleneimine units in the aforementioned skeleton moiety is preferably 10 or more, and  
35 is preferably in the range of 20 to 10,000.

[0021]

The polymer employed in the present invention may have the aforementioned straight-chain polyethyleneimine skeleton in the structure thereof. Even if the polymer is in the form of a line, a star, or a comb, a crystal can be provided in water or in an aqueous medium of a mixture of water and an aqueous organic solvent.

[0022]

In addition, the polymer in the form of a line, a star, or a comb may consist of only the straight-chain polyethyleneimine skeleton, or may be formed from a block copolymer between a block composed of a straight-chain polyethyleneimine skeleton (hereinafter, referred to as "polyethyleneimine block") and other polymer blocks. As other polymer blocks, for example, a water-soluble polymer block such as polyethylene glycol, polypropionyl ethyleneimine, or polyacrylamide, or a hydrophobic polymer block such as polystyrene, a polyoxazoline such as polyphenyl oxazoline, polyoctyl oxazoline, or polydodecyl oxazoline, or a polyacrylate such as a polymethyl methacrylate, or polybutyl methacrylate can be employed. By forming a block copolymer with the other aforementioned polymer blocks, forms or properties of the polymer crystals can be adjusted.

[0023]

When the polymer having the straight-chain polyethyleneimine skeleton is a block copolymer, the ratio of the straight-chain polyethyleneimine skeleton in the aforementioned polymer is not particularly limited as long as a polymer crystal can be formed. In order to suitably form the polymer crystal, the ratio of the straight-chain polyethyleneimine skeleton in the polymer is preferably not less than 40% by mol, and is further preferably not less than 50% by mol.

[0024]

The aforementioned polymer having the straight-chain polyethyleneimine skeleton can be easily produced by

hydrolyzing a polymer having a straight-chain skeleton formed from a polyoxazoline which is a precursor thereof (hereinafter, referred to as a precursor polymer) under an acidic condition or an alkaline condition. Therefore, the form of the polymer having the straight-chain polyethyleneimine skeleton, such as a line, a star, or a comb can be easily designed by controlling the form of the precursor polymer. In addition, the degree of polymerization and the terminal structure can be easily adjusted by controlling the degree of polymerization of the precursor polymer and terminal functional groups thereof. In addition, in the case of forming the block copolymer having the straight-chain polyethyleneimine skeleton, the block copolymer can be produced by employing the precursor polymer as a block copolymer, and selectively hydrolyzing the straight-chain skeleton formed from the polyoxazoline in the aforementioned precursor.

[0025]

The precursor polymer can be synthesized by means of a synthesis method such as a cation type polymerization method or a macromonomer method with a monomer of an oxazoline. By appropriately selecting a synthesis method or an initiator, the precursor polymers in any form of a line, a star, or a comb can be synthesized.

[0026]

As a monomer forming a straight-chain skeleton formed from a polyoxazoline, an oxazoline monomer such as methyloxazoline, ethyloxazoline, methylvinylloxazoline, phenyloxazoline, or the like, can be employed.

[0027]

As a polymerization initiator, a compound having a functional group such as an alkyl chloride group, an alkyl bromide group, an alkyl iodide group, a toluenesulfonyloxy group, or a trifluoromethylsulfonyloxy group can be employed.

The polymerization initiators can be obtained by converting the hydroxyl groups in various alcohol compounds into other

functional groups. In particular, as the functional group conversion, bromination, iodination, toluenesulfonation, or trifluoromethylsulfonation is preferable since the efficacy of the polymerization initiation is increased. In

5 particular, alkyl bromide and alkyl toluenesulfonate are preferable.

[0028]

In addition, as the polymerization initiator, a product in which the terminal hydroxyl group of a  
10 polyethylene glycol is substituted with a bromide or an iodide, or alternatively with a toluenesulfonyl group can also be employed. In this case, the degree of polymerization of the polyethylene glycol preferably ranges from 5 to 100, and in particular, preferably ranges from 10  
15 to 50.

[0029]

In addition, a pigment having a functional group having the ability of initiating a cation ring-opening living polymerization, and having any one of skeletons of a  
20 porphyrin skeleton, a phthalocyanine skeleton, and a pyrene skeleton, which has electron transfer functions, energy transfer functions, or luminescence functions caused by light, can provide specific functions to the obtained polymer.

25 [0030]

The linear precursor polymer can be obtained by polymerizing the aforementioned oxazoline monomer with a polymerization initiator having a monovalent or divalent functional group. As examples of the polymerization  
30 initiators, mention may be made of, for example, a monovalent initiator such as methylbenzene chloride, methylbenzene bromide, methylbenzene iodide, methylbenzene toluenesulfonate, methylbenzene trifluoromethylsulfonate, methane bromide, methane iodide, methane toluenesulfonate or  
35 toluenesulfonic anhydride, trifluoromethylsulfonic anhydride, 5-(4-bromomethylphenyl)-10,15,20-tri(phenyl)porphyrin, or

bromomethylpyrene, or a divalent initiator such as dibromomethylbenzene, methylbenzene diiodide, dibromomethylbiphenylene, or dibromomethylazobenzene. In addition, a linear polyoxazoline such as  
5 poly(methyloxazoline), poly(ethyloxazoline), or poly(methylvinylloxazoline), which is industrially used can be employed, as it is, as a precursor polymer.

[0031]

The precursor polymer in the form of a star can be  
10 obtained by polymerizing the oxazoline monomer as described above with a polymerization initiator having a functional group with not less than 3 valences. As examples of the polymerization initiator having not less than 3 valences, mention may be made of, for example, a trivalent  
15 polymerization initiator such as tribromomethylbenzene, a tetravalent polymerization initiator such as tetrabromomethylbenzene, tetra(4-chloromethylphenyl)porphyrin, or tetrabromoethoxy-phthalocyanine, or a polymerization initiator having 5 or  
20 more valences such as hexabromomethylbenzene, tetra(3,5-ditosylylethyloxyphenyl)porphyrin, or the like.

[0032]

In order to obtain a precursor polymer in the form of a comb, the oxazoline monomer can be polymerized with a  
25 linear polymer having a polyvalent polymerization initiating group, from the aforementioned polymerization initiating group. For example, the hydroxyl group of the polymer having a hydroxyl group at the side chain, such as a conventional epoxy resin or polyvinyl alcohol is halogenated  
30 with bromine, iodine, or the like, or alternatively is converted into a toluenesulfonyl group. Subsequently, the aforementioned converted moiety can also be employed as a polymerization initiating group.

[0033]

35 In addition, as a method for obtaining a precursor polymer in the form of a comb, a polyamine type



polymerization stopper can also be employed. For example, an oxazoline is polymerized with a monovalent polymerization initiator, and the terminal of the obtained polyoxazoline is bonded to an amino group of a polyamine such as

5 polyethyleneimine, polyvinylamine, polypropylamine, or the like. Thereby, the polyoxazoline in the form of a comb can be obtained.

[0034]

Hydrolysis of the straight-chain skeleton formed from  
10 the polyoxazoline of the precursor polymer obtained above may be carried out under acidic conditions or under alkaline conditions.

In the hydrolysis under acidic conditions, for example, a hydrochloride salt of the polyethyleneimine can be  
15 obtained by stirring the polyoxazoline in an aqueous solution of hydrochloric acid while heating. The obtained hydrochloride salt is treated with an excess of aqueous ammonia, and thereby, crystalline powders of a basic polyethyleneimine can be obtained. The aqueous solution of  
20 hydrochloric acid employed may be a concentrated hydrochloric acid or an aqueous solution at a concentration of approximately 1 mol/L. In order to efficiently carry out hydrolysis, it is preferable that an aqueous solution of hydrochloric acid at a concentration of 5 mol/L be employed.  
25 In addition, the reaction temperature is preferably around 80°C.

[0035]

In the hydrolysis under alkaline conditions, the polyoxazoline can be converted into the polyethyleneimine  
30 with, for example, an aqueous solution of sodium hydroxide. After the reaction is carried out under alkaline conditions, the reaction mixture is cleansed by means of a dialysis membrane, and thereby, the excess of sodium hydroxide is removed. As a result, crystalline powders of the  
35 polyethyleneimine can be obtained. The concentration of sodium hydroxide employed may range from 1 to 10 mol/L, and

preferably ranges from 3 to 5 mol/L in order to efficiently carry out the reaction. In addition, the reaction temperature is preferably around 80°C.

[0036]

5       The amount of the acid or alkali employed in the hydrolysis under acidic conditions or under alkaline conditions may range from 1 equivalent to 10 equivalents per oxazoline unit in the polymer, and is preferably around three equivalents in order to improve reaction efficacy and  
10       simplify after-treatments.

[0037]

By means of the aforementioned hydrolysis, the straight-chain skeleton composed of the polyoxazoline in the precursor polymer is converted into the straight-chain  
15       polyethyleneimine skeleton. Thereby, the polymer having the aforementioned polyethyleneimine skeleton can be obtained.

[0038]

In addition, in the case of forming a block copolymer between the straight-chain polyethyleneimine block and  
20       another polymer block, the block copolymer formed from the straight-chain polymer block composed of the polyoxazoline and another polymer block is employed as the precursor polymer, and the straight-chain block composed of the polyoxazoline in the aforementioned precursor polymer can be  
25       selectively hydrolyzed.

[0039]

When the other polymer block is a water-soluble polymer block such as poly(N-propionylethyleneimine) or the like, a block copolymer can be formed by utilizing the  
30       higher solubility of poly(N-propionylethyleneimine) in an organic solvent than that of poly(N-formylethyleneimine) or poly(N-acetyleneimine). In other words, after 2-oxazoline or 2-methyl-2-oxazoline is subjected to a cation ring-opening living polymerization in the presence of the  
35       aforementioned polymerization initiating compound, 2-ethyl-2-oxazoline is further polymerized to the obtained living

polymer. Thereby, a precursor polymer composed of a poly(N-formylethylenimine) block or a poly(N-acetylenimine) block and a poly(N-propionylethylenimine) block is obtained. The aforementioned precursor polymer is dissolved in water, and an organic solvent which is not compatible with water and is for dissolving the poly(N-propionylethylenimine) block is mixed and stirred with the aforementioned aqueous solution, thus producing an emulsion. By adding an acid or an alkali to the aqueous phase of the aforementioned emulsion, the poly(N-formylethylenimine) block or the poly(N-acetylenimine) block is preferentially hydrolyzed. Thereby, a block copolymer having the straight-chain polyethylenimine block and the poly(N-propionylethylenimine) block can be formed.

[0040]

When the number of the valence of the polymerization initiating compound employed here is one or two, a straight-chain block copolymer is obtained. When the number of the valence thereof is three or more, a block copolymer in the form of a star can be obtained. In addition, by employing a multiple-stage block copolymer as the precursor polymer, the obtained polymer can also have a multiple-stage block structure.

[0041]

#### Polymer Crystal

The aforementioned polymer having the polyethylenimine skeleton forms a polymer crystal by exhibiting crystalline properties in water or in a mixed solution of water and a hydrophilic solvent by the straight-chain polyethylenimine skeleton in the primary structure. The aforementioned polymer crystals can also form a hydrogel having a three-dimensional network structure by physical binding of the polymer crystals in the presence of water. In addition, the aforementioned polymer crystals can also form a crosslinked hydrogel having a chemically crosslinked bond by naturally crosslinking the polymer

crystals with a crosslinker.

[0042]

A polyethyleneimine which has been widely employed heretofore is a branched polymer obtained by means of ring-opening polymerization of a cyclic ethyleneimine, and in a primary structure thereof, there are a primary amine, a secondary amine, and a tertiary amine. Therefore, the branched polyethyleneimine is water-soluble, but does not have crystallizing properties. For this reason, in order to produce a hydrogel by employing the branched polyethyleneimine, a network structure must be provided by means of covalent bonding with a crosslinker. However, the straight-chain polyethyleneimine which the polymer employed in the present invention has as a skeleton is composed of only a secondary amine, and the aforementioned secondary amine type straight-chain polyethyleneimine is water-soluble, but exhibits superior crystalline properties.

[0043]

In the crystals of the straight-chain polyethyleneimine, it is known that polymer crystal structures greatly vary depending on the crystallization water molecules included in the ethyleneimine unit of the polymer (see Y. Chatani et al., *Macromolecules*, 1981, vol. 14, pp. 315-321). It is known that in an anhydrous polyethyleneimine, a crystal structure characterized by a double-helical structure prevails, and when two molecules of water are present in the monomer unit, the polymer forms a crystal characterized by a zigzag structure. In fact, the crystal of the straight-chain polyethyleneimine obtained in water is a crystal having two molecules of water per monomer unit, and is insoluble in water at room temperature.

[0044]

The polymer crystal of the polymer having the straight-chain polyethyleneimine skeleton in the present invention is formed in the same manner as that of the aforementioned case, by occurrence of crystallization of the

straight-chain polyethyleneimine skeleton. Even if the polymer is in the form of a line, a star, or a comb, a polymer crystal can be obtained as long as the polymer has the straight-chain polyethyleneimine skeleton as the primary structure.

[0045]

The presence of the polymer crystal in the present invention can be confirmed by means of X-ray scattering, and by the peaks assigned by the straight-chain polyethyleneimine skeleton in the crystal hydrogel at approximately 20°, 27°, and 28° of 2θ angle values in a wide-angle X-ray diffractometer (WAXS).

[0046]

In addition, the melting point of the polymer crystal in the present invention measured by a differential scanning calorimeter (DSC) depends on the primary structure of the polymer of the polyethyleneimine skeleton. In general, the melting point ranges from 45°C to 90°C.

[0047]

The polymer crystals in the present invention can be in various forms, in accordance with geometrical forms or molecular weight of the polymer structures forming the aforementioned crystals, the non-ethyleneimine moiety introducible in the primary structure, and conditions of forming the polymer crystals. For example, the polymer crystals have a form of a filament, a brush, a star or the like.

[0048]

The aforementioned polymer crystal is based on a polymer crystal in the form of a filament of nanometer order ranging from about 5 to 30 nm (hereinafter, the aforementioned crystal is referred to as filament nanocrystal). By the free ethyleneimine chain present on the surface of the aforementioned filament nanocrystal, filament nanocrystals are mutually linked by means of a physical bond due to a hydrogen bond, are arranged in the

space, and grow to the three-dimensional form as described above. The aforementioned polymer crystals are further physically bonded to form a crosslinked structure, and thereby, a three-dimensional network structure of the  
5 aforementioned polymer crystals is formed. They are formed in the presence of water, and for this reason, as a result, a hydrogel in which water is included in the aforementioned three-dimensional structure is formed.

[0049]

10 The three-dimensional network structure mentioned herein means a network structure formed by a physical crosslinking of polymer crystals of micro-scale or nano-scale themselves by virtue of hydrogen bonding of the free ethyleneimine chains present on the surface thereof,  
15 which is different from a conventional polymer hydrogel. Therefore, at temperatures of not lower than the melting point of the crystal, the crystal is dissolved in water, and the three-dimensional network structure is also destructured. However, if the temperature is turned to room temperature,  
20 the polymer crystals grow, and a physical crosslinking due to a hydrogen bonding between the crystals is formed. For this reason, a three-dimensional network structure is again observed.

[0050]

25 The polymer crystals of the present invention can be obtained by means of dissolution-crystallization conversion in water of the polymer having the aforementioned straight-chain polyethyleneimine skeleton by utilizing the property in which the  
30 polymer having the straight-chain polyethyleneimine skeleton is insoluble in water.

[0051]

In addition, a hydrogel can be obtained by, first, dispersing the polymer having the straight-chain  
35 polyethyleneimine skeleton, in a specified amount, in water, heating the aforementioned dispersion, to form a transparent

aqueous solution of the polymer having the polyethyleneimine skeleton, and subsequently cooling the aqueous solution of the heated polymer to room temperature. The aforementioned hydrogel may be deformed by exerting an external force such as a shearing force or the like, and can be deformed into various forms since it has a state such as ice cream which can maintain a general form.

[0052]

The heating temperature of the aforementioned polymer dispersion is preferably not higher than 100°C, and more preferably ranges from 90 to 95°C. In addition, the amount of the polymer included in the polymer dispersion is not particularly limited as long as a hydrogel can be obtained. The amount preferably ranges from 0.01 to 20% by weight, and further preferably ranges from 0.1 to 10% by weight in order to obtain a hydrogel composed of crystals having a stable form. As described above, in the present invention, if the polymer having the straight-chain polyethyleneimine skeleton is employed, a hydrogel can be formed even with a very small concentration of the polymer.

[0053]

By decreasing the temperature of the aqueous solution of the aforementioned polymer to room temperature, the crystal form in the obtained hydrogel can be adjusted. For example, the aqueous solution of the polymer is maintained for one hour at 80°C, is cooled to 60°C over one hour, is maintained for one hour at the aforementioned temperature, is subsequently cooled to 40°C over one hour, and is cooled naturally to room temperature. Thereby, a hydrogel crystal in the condition that water of the aqueous solution lacks fluidity can be obtained. In addition, the aforementioned aqueous solution of the polymer is, at once, cooled in ice-cooled water at a freezing point or in a refrigerant liquid of methanol with dry ice or acetone with dry ice at a temperature of not higher than the freezing point, and subsequently, the cooled solution is maintained in a water

bath at room temperature. Thereby, a hydrogel crystal can be obtained. Furthermore, the aforementioned aqueous solution of the polymer is cooled to room temperature in a water bath at room temperature or in air at room temperature.

5 Thereby, a hydrogel crystal can be obtained.

[0054]

The step of decreasing the temperature of the aqueous solution of the aforementioned polymer strongly effects on the form of the polymer crystals themselves in the  
10 obtained hydrogel. For this reason, the crystal morphology of the polymer in the hydrogel is not the same as that in the hydrogel obtained by the different aforementioned method.

[0055]

15 In the case of stepwisely decreasing the temperature of the aqueous solution of the aforementioned polymer in a specified concentration, the crystal morphology of the polymer in the hydrogel can be a polymer crystal morphology in the form of a fiber. When the fibers are immediately  
20 cooled, and then are returned to room temperature, a polymer crystal morphology in the form of a petal can be obtained. In addition, when the petal-shaped one is again cooled immediately in acetone with dry ice, and is returned to room temperature, a polymer crystal morphology in the form of a  
25 wave can be obtained. As described above, the crystal morphologies of the polymer in the hydrogel of the present invention can be specified to any form.

[0056]

The hydrogel obtained as described above is an opaque  
30 gel, and in the gel, crystals of the polymer having the polyethyleneimine skeleton are formed. The crystals themselves are physically crosslinked by hydrogen bonding, and a three-dimensional physical network structure is formed. The polymer crystals once formed  
35 in the hydrogel can maintain a non-soluble state at room temperature, but they can be changed into a sol state by



dissociation of the polymer crystals when they are heated. Therefore, the physical hydrogel of the present invention can be reversibly changed from a sol to a gel or from a gel to a sol by carrying out a heat treatment.

5 [0057]

The hydrogel mentioned in the present invention includes at least water in the three-dimensional network structure. A hydrogel including an organic solvent can be obtained by adding a water-soluble organic solvent during  
10 preparation of the aforementioned hydrogel. As examples of the aforementioned hydrophilic organic solvents, mention may be made of, for example, water-soluble organic solvents such as methanol, ethanol, tetrahydrofuran, acetone, dimethylacetamide, dimethylsulfoxide, dioxirane, pyrrolidone,  
15 and the like.

[0058]

The amount of the organic solvent preferably ranges from 0.1 to 5 times the volume of water, and more preferably ranges from 1 to 3 times the volume of water.

20 [0059]

By including the aforementioned hydrophilic organic solvent, the morphology of the polymer crystal can be changed, and crystals having a morphology which is different from that obtained from a simple aqueous  
25 system can be provided. For example, even if a branched crystal morphology which has a fibrous spread in water is exhibited, a spherical crystal morphology in which fibers are shrunk can be obtained in the case of a specified amount of ethanol during preparation  
30 thereof.

[0060]

By adding another water-soluble polymer during preparation of the hydrogel mentioned in the present invention, a hydrogel including a water-soluble polymer can  
35 be obtained. As examples of the aforementioned water-soluble polymer, mention may be made of, for example,

polyethylene glycol, polyvinyl alcohol, polyvinylpyrrolidone, polyacrylamide, poly(N-isopropylacrylamide), polyhydroxyethyl acrylate, polymethyloxazoline, polyethyloxazoline, and the like.

5 [0061]

The amount of the water-soluble polymer preferably ranges from 0.1 to 5 times the weight of the polymer having the straight-chain polyethyleneimine skeleton, and more preferably ranges from 0.5 to 2 times the weight of the  
10 polymer.

[0062]

Even by including the aforementioned water-soluble polymer, the morphology of the polymer crystals can be changed, and a crystal morphology which is different  
15 from the morphology obtained in a simple aqueous system can be provided. In addition, it is effective for increasing the viscosity of the hydrogel, and improving stability of the hydrogel.

[0063]

20 In addition, by treating the hydrogel obtained by the aforementioned method with a compound including not less than two functional groups which can react with the amino group of the polyethyleneimine, a crosslinked hydrogel in which the surfaces of the polymer crystals themselves are  
25 linked by chemical bonding in the hydrogel can be obtained.

[0064]

As the aforementioned compound including not less than two functional groups which can react with the  
30 aforementioned amino group at room temperature, an aldehyde crosslinker, an epoxy crosslinker, an acid chloride, an acid anhydride, or an ester crosslinker can be employed. As examples of the aldehyde crosslinker, mention may be made of, for example, malonyl aldehyde, succinyl aldehyde, glutaryl  
35 aldehyde, adipoyl aldehyde, phthaloyl aldehyde, isophthaloyl aldehyde, terephthaloyl aldehyde, and the like. In addition,

as examples of the epoxy crosslinker, mention may be made of, for example, polyethylene glycol diglycidyl ether, bisphenol A diglycidyl ether, glycidyl chloride, glycidyl bromide, and the like. As examples of the acid chloride, mention may be made of, for example, malonyl chloride, succinyl chloride, glutaryl chloride, adipoyl chloride, phthaloyl chloride, isophthaloyl chloride, terephthaloyl chloride, and the like. In addition, as examples of the acid anhydride, mention may be made of, for example, phthalic anhydride, succinic anhydride, glutaric anhydride, and the like. In addition, as examples of the ester crosslinker, mention may be made of methyl malonate, methyl succinate, methyl glutarate, methyl phthalate, methyl polyethylene glycol carbonate, and the like.

[0065]

The crosslinking reaction may be carried out by a method in which the obtained hydrogel is immersed in a solution of a crosslinker, or a method in which a solution of a crosslinker is added to the hydrogel. In the crosslinking reaction, the crosslinker permeates into the inside of the hydrogel, together with changes in osmotic pressure in the system, and the crystals themselves are linked thereto by hydrogen bonding, thus causing a chemical reaction with the nitrogen atom of ethyleneimine.

[0066]

The crosslinking reaction proceeds due to a reaction with the free ethyleneimine on the surface of the polyethyleneimine crystals. In order to avoid an occurrence of the aforementioned reaction at the inside of the crystals, the reaction is preferably carried out at a temperature of not higher than the melting point of the crystals for forming the hydrogel, and the crosslinking reaction is most preferably carried out at room temperature.

[0067]

When the crosslinking reaction is carried out at room temperature, the hydrogel is allowed to stand under the

condition of mixing with a solution of the crosslinker, and thereby, a crosslinked hydrogel can be obtained. The period of the crosslinking reaction may range from several minutes to several days. In general, the crosslinking suitably proceeds by leaving to stand overnight.

[0068]

The amount of the crosslinker may range from 0.05 to 20% with respect to moles of the ethyleneimine unit in the polymer having the polyethyleneimine skeleton employed in the formation of the hydrogel, and more preferably ranges from 1 to 10%.

[0069]

The aforementioned hydrogel can exhibit a gel structure with a variety of morphologies since the gelling agent is a crystalline polymer. In addition, even with a small amount of the polymer crystal, a three-dimensional network structure is suitably formed in water. For this reason, increased water-retaining properties can be exhibited. In addition, the employed polymer having the straight-chain polyethyleneimine skeleton is easily designed in view of the structure and is easily synthesized, and it is easy to prepare a hydrogel. In addition, by crosslinking between the polymer crystals in the aforementioned hydrogel with a crosslinker, the form of the hydrogel can be fixed.

[0070]

#### Hybrid

A hybrid between the aforementioned polymer crystal and the silica can be easily obtained by adding a solution in which a silica source is dissolved in a solvent usable in a common sol-gel reaction in a dispersion of the aforementioned polymer crystal in water or a hydrogel of the polymer crystal, and subjecting the mixture to a sol-gel reaction at room temperature.

[0071]

As examples of compounds employed as the silica source,

mention may be made of a tetraalkoxysilane, an alkyltrialkoxysilane, and the like.

[0072]

As examples of tetraalkoxysilanes, mention may be made of, for example, tetramethoxysilane, tetraethoxysilane, tetrapropoxysilane, tetrabutoxysilane, tetra-t-butoxysilane, and the like.

[0073]

As examples of alkyltrialkoxysilanes, mention may be made of methyltrimethoxysilane, methyltriethoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, n-propyltrimethoxysilane, n-propyltriethoxysilane, isopropyltrimethoxysilane, isopropyltriethoxysilane, 3-chloropropyltrimethoxysilane, 3-chloropropyltriethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, 3-glycyloxypropyltrimethoxysilane, 3-glycyloxypropyltriethoxysilane, 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-mercaptopropylmethoxysilane, 3-mercaptotriethoxysilane, 3,3,3-trifluoropropyltrimethoxysilane, 3,3,3-trifluoropropyltriethoxysilane, 3-methacryloxypropyltrimethoxysilane, 3-methacryloxypropyltriethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, p-chloromethylphenyltrimethoxysilane, p-chloromethylphenyltriethoxysilane, dimethyldimethoxysilane, dimethyldiethoxysilane, diethyldimethoxysilane, diethyldiethoxysilane, and the like.

[0074]

The aforementioned sol-gel reaction for providing a hybrid proceeds in an aqueous liquid such as water, a solvent mixture of water and a hydrophilic organic solvent, or the like, in the presence of the polymer crystal. The reaction does not occur in an aqueous liquid phase, and proceeds on the surface of the polymer. Therefore, the conditions of the hybrid reaction are not limited as long as the polymer crystals are not dissolved.

[0075]

In order to make the polymer crystal insoluble, in the sol-gel reaction, water is preferably present in not less than 20%, and is more preferably present in not less than 40%, in an aqueous liquid including the hydrophilic organic solvent.

[0076]

In the sol-gel reaction, if the amount of the alkoxysilane as a silica source is employed in excess with respect to the ethyleneimine which is the monomer unit of the polyethyleneimine, a hybrid can be suitably formed. The degree in excess of the alkoxysilane preferably ranges from 4 to 1,000 times equivalence of the ethyleneimine.

[0077]

In addition, the concentration of the polymer in the aqueous liquid during formation of the polymer crystal preferably ranges from 0.1 to 30% based on the amount of the polyethyleneimine included in the polymer.

[0078]

The period of the sol-gel reaction may vary from one minute to several days. In the case of employing a methoxysilane exhibiting high reactivity of the alkoxysilane, the reaction period may range from one minute to 24 hours, and in order to improve reaction efficiency, the reaction period is suitably set to range from 30 minutes to 5 hours. In addition, in the case of employing an ethoxysilane, or a butoxysilane exhibiting low reactivity, the period of the sol-gel reaction is preferably not less than 24 hours, and is more preferably about one week.

[0079]

The hybrids of the present invention have main characteristics that they have various forms. The form thereof is an enlarged copy of the form of the polymer crystal. Therefore, before the sol-gel reaction, first, the polymer crystal is grown in water or in an aqueous medium, and the form of the polymer crystal is adjusted. Thereby,

the form of the hybrid can be controlled. The preparation of the polymer crystal and the hydrogel derived from the polymer crystal in water or an aqueous liquid is as described above.

5 [0080]

The form of the obtained hybrid can be adjusted to various three-dimensional forms such as a lettuce, a fiber, a sponge, an aster, a cactus, a dandelion, and the like. The size of the aforementioned hybrids can be a micrometer  
10 order size in the range of from approximately 3  $\mu\text{m}$  to 1 mm. The form thereof is a three-dimensional form formed by the aggregation of the filament hybrid with a size ranging from 20 to 30 nm which may be a base unit, and the arrangement in space. In the filament hybrid having a size ranging from 20  
15 to 30 nm which may be the base unit, a core with approximately 5 nm is included. The core is a filament nanocrystal of the polymer having the straight-chain polyethyleneimine skeleton. Namely, it is considered that in the aforementioned three-dimensional form of micrometer  
20 order, the aforementioned filament nanocrystals are mutually linked by means of a physical bond due to a hydrogen bond in water and arranged in space to form a template in the various three-dimensional forms. The silica is fixed in accordance with the aforementioned template. Thereby,  
25 filament hybrids with a size ranging from 20 to 30 nm are mutually aggregated to form a morphology arranged in space.

[0081]

The aforementioned forms can be adjusted by the geometrical form of the polymer structure, the molecular  
30 weight thereof, the non-ethyleneimine moiety which can be introduced in the primary structure, the conditions of forming a polymer crystal and the like, as described above, and greatly depend on the molecular structure of the polymer employed, the degree of polymerization, the composition, and  
35 the method for lowering the temperature during preparation of the polymer crystals.

[0082]

For example, a hybrid having a three-dimensional form like a lettuce can be obtained by employing a linear polyethyleneimine having a degree of polymerization of not less than 300 as the polymer having the straight-chain polyethyleneimine skeleton, and decreasing the temperature naturally from not less than 80°C to room temperature to obtain a polymer crystal, followed by carrying out a sol-gel reaction with the aforementioned polymer crystal. The thickness of the leaf part in the hybrid in the form of a lettuce is increased as the concentration of the polymer in the polymer solution during crystallizing the polymer is decreased. When the concentration is not less than 2%, the thickness of the leaf part is approximately 100 nm. When the concentration is not more than 1%, the thickness of the leaf part is approximately 500 nm.

[0083]

In addition, in the case of employing a polyethyleneimine in the form of a star, the form of the hybrid obtained can also be controlled by changing the structure of a center residue which forms a nucleus thereof. For example, if the center residue has a large pi plane such as a porphyrin, the three-dimensional form of the obtained hybrid is an aster form, and the size of one crystal in the form of an aster ranges from approximately 2 to 6  $\mu\text{m}$ . If the concentration is not less than 1%, the number of the arms of the aster is small, and the arms tend to band together. If the concentration is below 1%, the number of the arms is large, and the arms tend to independently separate. In addition, if the center residue has a small structure such as a benzene ring, the obtained hybrid is in the form of a fiber in which many strings are banded together, and the fibers are mutually intertangled to form a three-dimensional hybrid in the overall form of a sponge. The diameter of one fiber form is approximately 150 nm.

[0084]



In addition, the hybrids in the various three-dimensional forms formed from the aggregation of the aforementioned filament hybrids and space arrangements are further aggregated, and thereby, a hybrid of a macro form with a size of millimeter order or greater can also be formed. This is obtained by linking fiber nanocrystals of the polymer having the linear polyethyleneimine skeleton in water or an aqueous liquid by means of a physical bond due to a hydrogen bond in water, arranging the fiber nanocrystals in space to form polymer crystals in various forms, forming a three-dimensional network structure by further physically binding the aforementioned polymers, fixing this by a silica, and thereby, forming a morphology in which hybrids having a three-dimensional form are mutually aggregated.

[0085]

In addition, by employing a crosslinked hydrogel in which the polymer crystals are crosslinked by means of chemical bonds, a macro form of the hybrid is controlled, and compacts in various forms can be obtained from the hybrids. The form and size thereof can be the same as the size and form of the container employed during preparation of the crosslinked hydrogel. For example, the compacts can be produced in any form such as a disk, a cylinder, a plate, a sphere, or the like. In addition, by cutting the crosslinked hydrogel, a desired form can also be obtained. The crosslinked hydrogel formed as described above is immersed in a solution of a silica source, and thereby, a compact composed of hybrids between the polymer crystals and the silica can be easily obtained. The period for immersing in the solution of the silica source varies from one hour to one week, depending on the type of the silica source employed. For this reason, it is necessary to appropriately adjust the period. In a solution of a methoxysilane, the period may range from approximately 1 hour to 48 hours. In a solution of an ethoxysilane, the period preferably ranges

from approximately 1 day to 7 days.

[0086]

Usually, the hybrid of the present invention is composed of the polymer crystals and the silica, and the amount of the silica in the hybrid varies within a specified range, depending on reaction conditions and the like, and can range from 30 to 90% by weight of the total weight of the hybrid.

The amount of the silica included increases in accordance with increasing the amount of the polyethyleneimine polymer employed in the sol-gel reaction, and namely, in accordance with increasing the concentration of the polymer in the hydrogel. In addition, the amount of the silica increases by increasing the period of the sol-gel reaction.

[0087]

The hybrids of the present invention have various forms as described above, and the forms can be divided into a primary form, a secondary form, and a tertiary form. As the primary form, the form is a filament hybrid having a size of nanometer order. As the secondary form, the size thereof is micrometer order. The form variously changes into tertiary forms such as a lettuce, a fiber, a sponge, an aster, a cactus, a dandelion, and the like, by adjusting the molecular structure of the polymer employed, the molecular weight thereof, the molecular composition, the crystal-forming conditions and the like. The forms are preferential and under specified conditions with a specified molecule, only one type of form can be obtained. The tertiary form is a macro form including the primary form and the secondary form, and the tertiary form can be shaped by various processing.

[0088]

In the hybrids of the present invention, nanocrystals of a polyethyleneimine are included in the inner part of a silica layer. A fluorescence substance can be introduced in

the aforementioned polymer. For example, by employing a polyethyleneimine in the form of a star based on porphyrin, the residue of porphyrin can be introduced in the hybrid. In addition, by employing a polymer crystal in which a pyrene such as pyrene aldehyde, in a small amount and preferably not more than 10% by mol with respect to the amount of imine, is reacted with the side chain of the polyethyleneimine, the pyrene residue can be introduced in the hybrid. In addition, by employing a mixture in which a fluorescence dye such as a porphyrin, a phthalocyanine, a pyrene, or the like, having an acidic group such as a carboxylic acid group, or sulfonic acid group, in a small amount and preferably not more than 0.1% by mol with respect to the number of moles of the imine, is mixed with the base of the polyethyleneimine, the fluorescence substance can be introduced in the hybrid in which the crystal can be used as a template.

[0089]

The hybrid of the present invention is a novel hybrid which the conventional difficulties of controlling forms at the time of producing a silica material are completely removed. The application thereof is largely expected regardless of categories of business or area. In addition, the hybrids of the present invention include filament nanocrystals composed of the polymer having the straight-chain polyethyleneimine skeleton in the inner part thereof. For this reason, the hybrids of the present invention are useful materials in not only areas to which silica materials are generally applied, but also areas to which polyethyleneimines are applied.

[EXAMPLES]

[0090]

In the following, the present invention is described in detail with reference to Examples and Reference Examples. It should be understood that the present invention is not limited to these examples. "%" means "% by weight", unless

otherwise indicated.

[0091]

Analysis of a hybrid by means of X-ray diffractometry

A hybrid which had been isolated and dried was mounted  
5 on a holder for measuring samples, and the holder was set on  
a wide-angle X-ray diffractometer "Rint-Ultma" manufactured  
by Rigaku Corporation. Measurement was carried out under  
the conditions of Cu/K $\alpha$  ray, 40 kV/30 mA, scanning speed of  
1.0°/min, and scanning range of 10 to 40°.

10 [0092]

Analysis of a hybrid by means of differential scanning  
calorimetry

A hybrid which had been isolated and dried was weighed  
by means of a measure patch, and was set on a differential  
15 scanning calorimeter "DSC-7" manufactured by Perkin Elmer  
Co., Ltd. Measurement was carried out at a rate of  
increasing temperature of 10°C/min in a temperature range of  
from 20°C to 90°C.

[0093]

20 Morphological analysis of a hybrid by means of  
scanning electron microscopy

A hybrid which had been isolated and dried was mounted  
on a glass slide, and was then observed by means of a  
surface observing equipment "VE-7800" manufactured by  
25 Keyence Corporation.

[0094]

Observation of a hybrid by means of transmission  
electron microscopy

A hybrid which had been isolated and dried was mounted  
30 on a carbon-deposited copper grid, and was observed by means  
of a high-resolution electron microscope EM-002B, VOYAGER M  
3055, manufactured by Topcon Noran Instruments Co., Ltd.

[0095]

Synthesis Example 1

35 Synthesis of linear polyethyleneimine (L-PEI)

A commercially available polyethyloxazoline (number

average molecular weight = 500,000, mean degree of polymerization = 5,000, manufactured by Aldrich Corp.), in an amount of 5 g, was dissolved in 20 mL of a 5 M aqueous solution of hydrochloric acid. The solution was heated to 90°C in an oil bath, and was stirred for 10 hours at the same temperature. Acetone, in an amount of 50 mL, was added to the reaction mixture to completely precipitate a polymer. The polymer was filtered, and washed with methanol three times. As a result, a white powder of polyethyleneimine was obtained. The obtained powder was identified by means of  $^1\text{H-NMR}$  (deuterated water). As a result, it was confirmed that the peaks at 1.2 ppm ( $\text{CH}_3$ ) and 2.3 ppm ( $\text{CH}_2$ ) assigned to the ethyl group of the side chain of the polyethyloxazoline completely disappeared. In other words, this result indicated that the polyethyloxazoline was completely hydrolyzed and was converted into a polyethyleneimine.

[0096]

The powder was dissolved in 5 mL of distilled water, and 50 mL of 15% aqueous ammonia was added dropwise to the aforementioned solution while being stirred. The mixture was allowed to stand overnight. Subsequently, precipitated powder was filtered, and the powder was washed with cooled water three times. The washed powder was dried in a desiccator at room temperature, and thereby, a linear polyethyleneimine (L-PEI) was obtained. The yield was 4.2 g (including crystallization water). In the polyethyleneimine obtained by hydrolyzing the polyoxazoline, only the side chain thereof was reacted, and the main chain was not changed. Therefore, the degree of polymerization of the L-PEI was 5,000, and was the same as that before hydrolysis.

[0097]

#### Synthesis Example 2

Synthesis of polyethyleneimine having porphyrin as the center in the form of a star (P-PEI)

In accordance with the method described in Jin et al.,

J. Porphyrin & Phthalocyanine, 3, 60 - 64 (1999); and Jin, Macromol. Chem. Phys., 204, 403 - 409 (2003), a polymethyloxazoline having a center of porphyrin in the form of a star as a precursor polymer was synthesized as described below.

[0098]

The inside of a two-neck flask with a volume of 50 mL equipped with a three-way tap was displaced with an argon gas. Subsequently, 0.0352 g of tetra(p-

10 iodomethylphenyl)polyoxazoline (TOMPP), and 8.0 mL of N,N-dimethylacetamide were added thereto. The mixture was stirred at room temperature, and TIMPP was completely dissolved. To the solution, 2-methyl-2-oxazoline, in an amount of 3.4 mL (3.27 g), corresponding to 1,280 times the  
15 moles of the porphyrin was added. Subsequently, the temperature of the reaction mixture was increased to 100°C, and was stirred for 24 hours. The reaction mixture was cooled to room temperature, and 10 mL of methanol was then added thereto. Subsequently, the mixture was concentrated  
20 under reduced pressure. The residue was dissolved in 15 mL of methanol, and the solution was poured into 100 mL of tetrahydrofuran. Thereby, a polymer was precipitated. In the same manner as described above, the polymer was again precipitated, and was subjected to suction filtration.

25 Subsequently, the polymer obtained was placed in a desiccator with P<sub>2</sub>O<sub>5</sub>, and was subjected to suction drying for one hour by means of an aspirator. In addition, the polymer was dried for 24 hours under vacuum by means of a vacuum pump, thus producing a precursor polymer. Yield was  
30 3.05 g (92.3%).

[0099]

The number average molecular weight of the precursor polymer (TPMO-P) obtained, which was measured by means of GPC, was 28,000, and the molecular weight distribution was  
35 1.56. In addition, the integral ratio of the ethylene proton at the polymer arm and the pyrrole cyclic proton of

porphyrin at the center of the polymer was calculated. As a result, the average degree of polymerization of each of the arms was 290. Therefore, the number average molecular weight based on  $^1\text{H-NMR}$  was assumed as 99,900. Great surpassing of the value of the number average molecular weight based on  $^1\text{H-NMR}$  with respect to the value of the number average molecular weight based on GPC is consistent with a general characteristic in a polymer in the form of a star.

10 [0100]

Employing the aforementioned precursor polymer, the polymethyloxazoline was hydrolyzed in the same manner as that of the aforementioned Synthesis Example 1. Thereby, a polyethyleneimine (P-PEI) in the form of a star was obtained in which four polyethyleneimines were linked to the porphyrin as the center. As a result of measurement by  $^1\text{H-NMR}$  (TMS = external standard, in deuterated water), the peak at 1.98 ppm assigned by the methyl side chain of the precursor polymer before hydrolysis completely disappeared.

20 [0101]

#### Synthesis Example 3

Synthesis of polyethyleneimine having a benzene ring as the center in the form of a star (B-PEI)

In accordance with the method described in Jin, J. Mater. Chem., 13, 672 - 675 (2003), a polymethyloxazoline in the form of a star in which 6 arms of the polymethyloxazoline were linked to a center of a benzene ring which was a precursor polymer was synthesized as described below.

30 [0102]

In a test tube having a joint inlet formed by ground glass, to which a magnetic stirrer was set, 0.021 g (0.033 mmol) of hexakis(bromomethyl)benzene as a polymerization initiator was placed, and a three-way tap was set to the inlet of the test tube. Subsequently, in the test tube, the condition was set under vacuum, and then replacement with

nitrogen gas was carried out. Under a stream of nitrogen gas, 2.0 mL (24 mmol) of 2-methyl-2-oxazoline, and 4.0 mL of N,N-dimethylacetamide were successively added by means of a syringe from the inlet of the three-way tap. The test tube  
5 was heated to 60°C in an oil bath, and was maintained as it was for 30 minutes. As a result, the mixture was transparent. The transparent mixture was further heated to 100°C, and was stirred for 20 hours at the same temperature, thus obtaining a precursor polymer. From <sup>1</sup>H-NMR measurement  
10 of the mixture, the conversion ratio of the monomer was 98%. As a result of estimating the average degree of polymerization of the polymer based on the aforementioned conversion ratio, the average degree of polymerization of each of the arms was 115. In addition, in measurement of  
15 the molecular weight by means of GPC, the weight average molecular weight of the polymer was 22,700, and the molecular weight distribution was 1.6.

[0103]

Employing the aforementioned precursor polymer, a  
20 polymethyloxazoline was hydrolyzed in the same manner as that of the aforementioned Synthesis Example 1. Thereby, a polyethyleneimine B-PEI in the form of a star in which 6 polyethyleneimines were linked to the benzene ring core was obtained. As a result of measurement by means of <sup>1</sup>H-NMR  
25 (TMS = external standard, in deuterated water), the peak at 1.98 ppm assigned as the methyl side chain of the precursor polymer before hydrolysis completely disappeared.

[0104]

The obtained polymethyloxazoline in the form of a star  
30 was hydrolyzed in the same manner as that of the aforementioned Synthesis Example 1. Thereby, a polyethyleneimine (B-PEI) in the form of a star in which 6 polyethyleneimines were linked to the benzene ring core was obtained.

[0105]

Synthesis Example 4



### Synthesis of block copolymer PEG-b-PEI

A polymer in which tosylate was bonded to one terminal of a polyethylene glycol having a number average molecular weight of 4,000 was employed as a polymerization initiator (PEG-I), and a block copolymer between a polyethylene glycol as a precursor block polymer and a polyoxazoline was obtained as described below.

[0106]

In a test tube having a joint inlet formed by ground glass, to which a magnetic stirrer was set, 1.5 g (0.033 mmol) of PEG-I as a polymerization initiator was placed, and a three-way tap was set to the inlet of the test tube. Subsequently, in the test tube, the condition was set under vacuum, and then replacement with nitrogen gas was carried out. Under a stream of nitrogen gas, 6.0 mL (72 mmol) of 2-methyl-2-oxazoline, and 20.0 mL of N,N-dimethylacetamide were successively added by means of a syringe from the inlet of the three-way tap. The test tube was heated to 100°C in an oil bath, and was stirred for 24 hours at the same temperature. Thereby, a precursor block polymer was obtained. From  $^1\text{H}$ -NMR measurement of the obtained mixture, it could be seen that the conversion ratio of the monomer was 100%.

[0107]

Yield of the precursor block polymer after purification was 93%. In addition, in the  $^1\text{H}$ -NMR measurement, each of the integral ratios was obtained on the basis of the tosyl group present at the terminal of the polymer. The degree of polymerization of PEG was 45, and the degree of polymerization of polyoxazoline was 93. In other words, the average degree of polymerization of the block polymer was 138. In addition, in measurement of the molecular weight by means of GPC, the number average molecular weight of the polymer was 12,000, and the molecular weight distribution was 1.27.

[0108]

Employing the aforementioned precursor block polymer, a polyoxazoline was hydrolyzed in the same manner as that of the aforementioned Synthesis Example 1. Thereby, a block copolymer (PEG-b-PEI) in which polyethyleneimine was bonded to PEG was obtained. As a result of measurement by means of  $^1\text{H-NMR}$  (TMS = external standard, in deuterated water), the peak at 1.98 ppm assigned as the methyl of the side chain of the precursor polymer before hydrolysis completely disappeared.

[0109]

#### Example 1

Hybrid from a linear polyethyleneimine system

A specified amount of the L-PEI powder obtained in Synthesis Example 1 was weighed, and dispersed in distilled water to prepare an L-PEI dispersion having each of the various concentrations shown in Table 1. The dispersions were heated to 90°C in an oil bath, and thereby, completely transparent aqueous solutions having different concentrations were obtained. The aqueous solutions were allowed to stand at room temperature to cool naturally to room temperature. Thereby, opaque L-PEI hydrogels (11) to (15) were obtained. In the obtained hydrogels, deformation occurred by exerting a shearing force, but a general form thereof could be maintained. They were hydrogels in the form of ice cream.

[0110]

As a result of X-ray diffraction measurement for the obtained hydrogel (15), it was confirmed that at 20.7°, 27.6°, and 28.4°, scattering intensity peaks were observed. In addition, as a result of measurement of changes in endothermic conditions by means of a calorimetric analyzer, it was confirmed that an endothermic peak was observed at 64.7°C. From the measurement results, the presence of crystals of L-PEI in the hydrogel was confirmed.

[0111]

Table 1: Hybrids obtained with various L-PEI concentrations

No.	11	12	13	14	15
L-PEI concentration (%)	0.25	0.5	1.0	2.0	3.0
TMSO/EtOH (1/1) mL	1	1	2	2	2

## [0112]

To 1 mL of the hydrogel obtained above, 1 mL or 2 mL of a mixture of tetramethoxysilane (TMSO) and ethanol in 1/1 (volume ratio) was added as shown in Table 1, and the mixture in the form of ice cream was lightly stirred for one minute. Subsequently, the mixture was allowed to stand for 40 minutes as it was. Subsequently, the mixture was washed with an excess of acetone, and then was cleaned three times by means of a centrifuge. The obtained solid was recovered and dried at room temperature, thus obtaining each of hybrids 11 to 15. From X-ray diffraction measurement for hybrid structure 14, at 20.5°, 27.2°, and 28.2°, scattering intensity peaks were observed.

## [0113]

As a result of observation of the obtained hybrid by means of a scanning electron microscope, in each of hybrids 11 to 15, an aggregate form in the form of a lettuce was confirmed. A scanning electron micrograph of the obtained hybrid 14 is shown in Fig. 1. In addition, as a result of observation of the aforementioned hybrid 14 by means of a transmission electron microscope, it was confirmed that a silica covered over the surface of the polymer crystal having a diameter of approximately 5 nm, as shown in Fig. 2.

## [0114]

## Example 2

Hybrid employing a polyethyleneimine including a porphyrin in the form of a star

P-PEI hydrogels (21) to (25) having concentrations shown in Table 2 were obtained in the same manner as that of Example 1, employing P-PEI synthesized in Synthesis Example

2 instead of employing the L-PEI powder in Example 1. In the obtained hydrogels, deformation occurred by exerting a shearing force, but a general shape could be maintained. The hydrogels were in the form of ice cream.

[0115]

As a result of X-ray diffraction measurement for the obtained hydrogel (25), it was confirmed that at 20.4°, 27.3°, and 28.1°, scattering intensity peaks were observed. In addition, as a result of measurement of changes in endothermic conditions by means of a calorimetric analyzer, it was confirmed that an endothermic peak was observed at 64.1°C. From the measurement results, the presence of crystals of P-PEI in the hydrogel was confirmed.

[0016]

Table 2: Hybrids obtained from various P-PEI concentrations

No.	21	22	23	24	25
P-PEI concentration (%)	0.25	0.5	1.0	2.0	3.0
TMSO/EtOH (1/1) mL	1	1	2	2	2

[0117]

To 1 mL of the hydrogel obtained above, 1 mL or 2 mL of a mixture of tetramethoxysilane (TMSO) and ethanol in 1/1 (volume ratio) was added, and the mixture in the form of ice cream was lightly stirred for one minute. Subsequently, the mixture was allowed to stand for 40 minutes as it was. Subsequently, the mixture was washed with an excess of acetone, and was cleaned by means of a centrifuge three times. The obtained solid was recovered and dried at room temperature, thus obtaining hybrids 21 to 25. As a result of X-ray diffraction measurement for the obtained hydrogel 24, it was confirmed that at 20.5°, 27.4°, and 28.1°, the same scattering intensity peaks as those before covering with the silica were observed.

[0118]

As a result of observation of the obtained hybrid by means of a scanning electron microscope, in each of the hybrids 21 to 25, an aggregate form in the form of an aster was confirmed. A scanning electron micrograph of the obtained hybrid 24 is shown in Fig. 3.

[0119]

### Example 3

Hybrid employing polyethyleneimine having a benzene ring as a center

B-PEI hydrogels (31) to (35) having concentrations shown in Table 3 were obtained in the same manner as that of Example 1, employing B-PEI synthesized in Synthesis Example 3 instead of employing the L-PEI powder, in Example 3. In the obtained hydrogels, deformation occurred by exerting a shearing force, but a general shape could be maintained. The hydrogels were in the form of ice cream. The gelling temperatures of the obtained hydrogels are shown in Table 3.

[0120]

As a result of X-ray diffraction measurement for the obtained hydrogel (34), it was confirmed that at 20.3°, 27.3°, and 28.2°, scattering intensity peaks were observed. In addition, as a result of measurement of changes in endothermic conditions by means of a calorimetric analyzer, it was confirmed that an endothermic peak was observed at 55.3°C. From the measurement results, the presence of crystals of B-PEI in the hydrogel was confirmed.

[0121]

Table 3: Hybrids obtained from various B-PEI concentrations

No.	31	32	33	34	35
B-PEI concentration (%)	0.25	0.5	1.0	2.0	3.0
TMOS/EtOH (1/1) mL	1	1	2	2	2

[0122]

To 1 mL of the hydrogel obtained above, 1 mL or 2 mL

of a mixture of tetramethoxysilane (TMSO) and ethanol in 1/1 (volume ratio) was added, and the mixture in the form of ice cream was lightly stirred for one minute. Subsequently, the mixture was allowed to stand for 40 minutes as it was.

5 Subsequently, the mixture was washed with an excess of acetone, and was cleaned by means of a centrifuge three times. The obtained solid was recovered, and dried at room temperature, thus obtaining hybrids 31 to 35. As a result of X-ray diffraction measurement for the obtained hybrid 34,  
10 it was confirmed that at 20.5°, 27.5°, and 28.3°, scattering intensity peaks were observed.

[0123]

As a result of observation of the obtained hybrid by means of a scanning electron microscope, it was confirmed  
15 that each of the hybrids 31 to 35 was in the form of a sponge in which fibrous forms were gathered. A scanning electron micrograph of the obtained hybrid 34 is shown in Fig. 4.

[0124]

20 Example 4

Hydrogel employing a block polymer

A PEG-b-PEI hydrogel 41 having a concentration of 5% of PEG-b-PEI was obtained in the same manner as that of Example 1, employing the PEG-b-PEI synthesized in Synthesis  
25 Example 4 instead of employing the L-PEI powder in Example 1.

[0125]

To 1 mL of the hydrogel obtained above, 1.5 mL of a mixture of tetramethoxysilane (TMSO) and ethanol in 1/1 (volume ratio) was added, and the mixture in the form of ice  
30 cream was lightly stirred for one minute. Subsequently, the mixture was allowed to stand for 40 minutes as it was. Subsequently, the mixture was washed with an excess of acetone, and was cleaned by means of a centrifuge three times. The obtained solid was recovered, and dried at room  
35 temperature, thus obtaining hybrid 41 in the same manner as described in Example 1.

[0126]

As a result of observation of the obtained hybrid by means of a scanning electron microscope, the hybrid 41 was in the form of a cactus. A scanning electron micrograph of the obtained hybrid 34 is shown in Fig. 5.

[0127]

#### Example 5

Hybrid from a polyethyleneimine hydrogel including an organic solvent

Hydrogels (51) to (53) including organic solvents were obtained in the same manner as that of obtaining the hydrogel (14) of Example 1, with the exception of employing solution mixtures of water and organic solvents in which the organic solvents shown in Table 5 were added to water, instead of employing distilled water in Example 1. In the obtained hydrogel, deformation occurred by exerting a shearing force, but a general shape could be maintained. The hydrogel was in the form of ice cream.

[0128]

Table 4: Hybrid obtained from a hydrogel containing an organic solvent

No.	51	52	53
Organic solvent contained	Acetone	DMF	EtOH
Amount of the solvent employed (%)	25	25	25
L-PEI concentration (%)	1.0	1.0	1.0
TMOS/EtOH (1/1) mL	2	2	2

[0129]

To 1 mL of the hydrogel obtained above, 1 mL or 2 mL of a mixture of tetramethoxysilane (TMSO) and ethanol in 1/1 (volume ratio) was added as shown in Table 5, and the mixture in the form of ice cream was lightly stirred for one minute. Subsequently, the mixture was allowed to stand for 40 minutes as it was. Subsequently, the mixture was washed with an excess of acetone, and was cleaned by means of a centrifuge three times. The obtained solid was recovered

and dried at room temperature, thus obtaining hybrids 51 to 53.

[0130]

As a result of observation of the obtained hybrid by means of a scanning electron microscope, it was confirmed that the hybrids 51 to 53 had different aggregate forms. A scanning electron micrograph of the obtained hybrid 51 is shown in Fig. 6. A scanning electron micrograph of the obtained hybrid 52 is shown in Fig. 7. A scanning electron micrograph of the obtained hybrid 53 is shown in Fig. 8.

[0131]

#### Example 6

Hybrid from a hydrogel of polyethyleneimine crosslinked by a dialdehyde

The hydrogel (15) having a concentration of 3% of L-PEI prepared in Example 1 was formed into a plate, and was added to 10 mL of an aqueous solution (5%) of glytaryl aldehyde. The mixture was allowed to stand for 24 hours at room temperature. The hydrogel before chemically crosslinking was in the form of ice cream, and could freely change the shape by means of a shearing force. In contrast, the hydrogel obtained by a chemically-crosslinking treatment became one aggregate, and changes in the shape thereof by means of a shearing force did not occur.

[0132]

The aforementioned plate was immersed in 2 mL of a mixture of TMOS/EtOH (1/1) for 24 hours. The plate was immersed in acetone repeatedly, and was washed. Thereby, a hybrid 61 was obtained.

[0133]

A scanning electron micrograph of the plate of the obtained hybrid 61 is shown in Fig. 9. A scanning electron micrograph of the surface of the plate of the aforementioned hybrid is shown in Fig. 10.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[0134]



[Fig. 1] Fig. 1 is a micrograph of a scanning electron microscope of a hybrid in the form of a lettuce in Example 1 of the present invention.

5 [Fig. 2] Fig. 2 is a micrograph of a transmission electron microscope of a polymer crystal covered with a silica in the hybrid in the form of a lettuce in Example 1 of the present invention.

10 [Fig. 3] Fig. 3 is a micrograph of a scanning electron microscope of a hybrid in the form of an aster in Example 2 of the present invention.

[Fig. 4] Fig. 4 is a micrograph of a scanning electron microscope of a hybrid in the form of a fibrous sponge in Example 3 of the present invention.

15 [Fig. 5] Fig. 5 is a micrograph of a scanning electron microscope of a hybrid in the form of a cactus in Example 4 of the present invention.

[Fig. 6] Fig. 6 is a micrograph of a scanning electron microscope of a hybrid obtained from a system including acetone in Example 5 of the present invention.

20 [Fig. 7] Fig. 7 is a micrograph of a scanning electron microscope of a hybrid obtained from a system including DMF in Example 5 of the present invention.

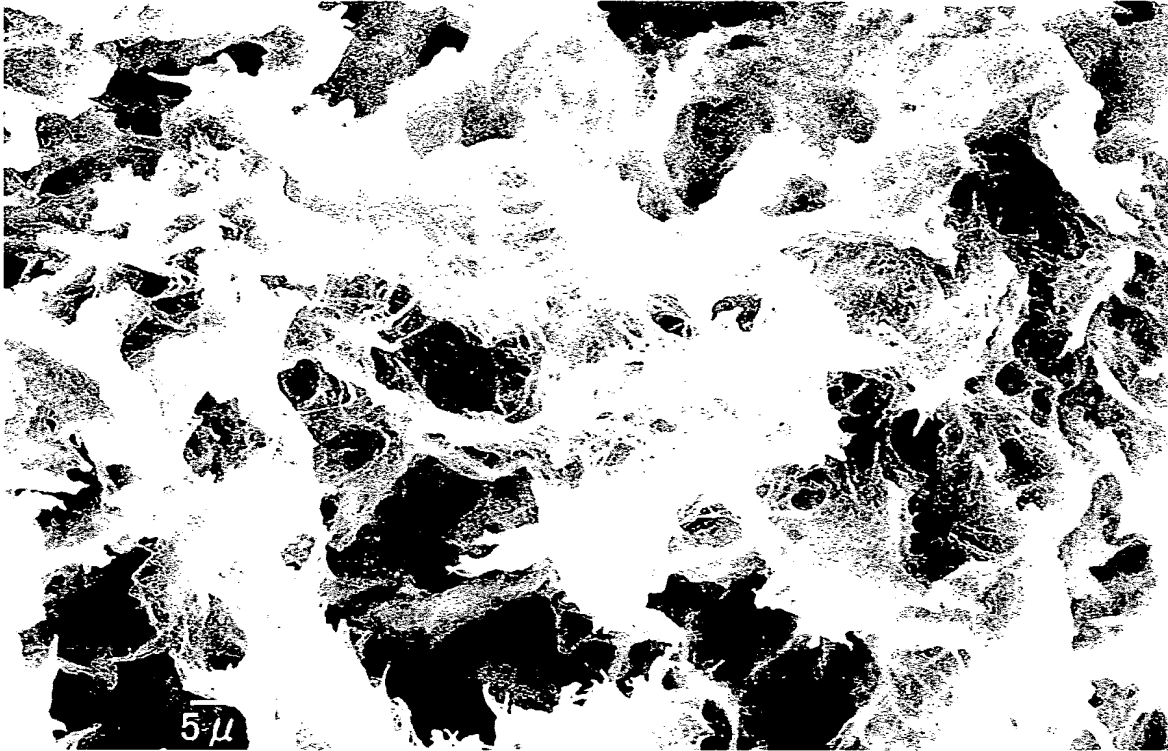
[Fig. 8] Fig. 8 is a micrograph of a scanning electron microscope of a hybrid obtained from a system including ethanol in Example 5 of the present invention.

25 [Fig. 9] Fig. 9 is a micrograph of a scanning electron microscope of a hybrid obtained from a system crosslinked by a chemical bond in Example 6 of the present invention.

30 [Fig. 10] Fig. 10 is a micrograph of a scanning electron microscope of a plate surface of a hybrid obtained from a system crosslinked by a chemical bond in Example 6 of the present invention.

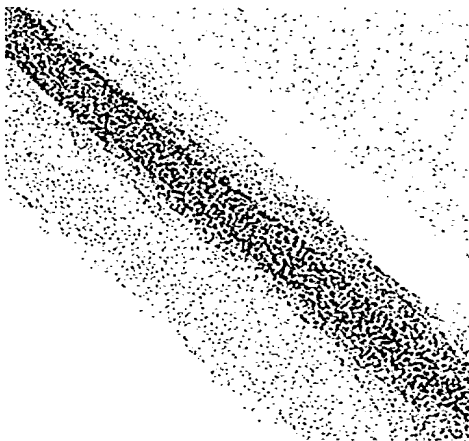
[Document Name] DRAWINGS

[Fig. 1]

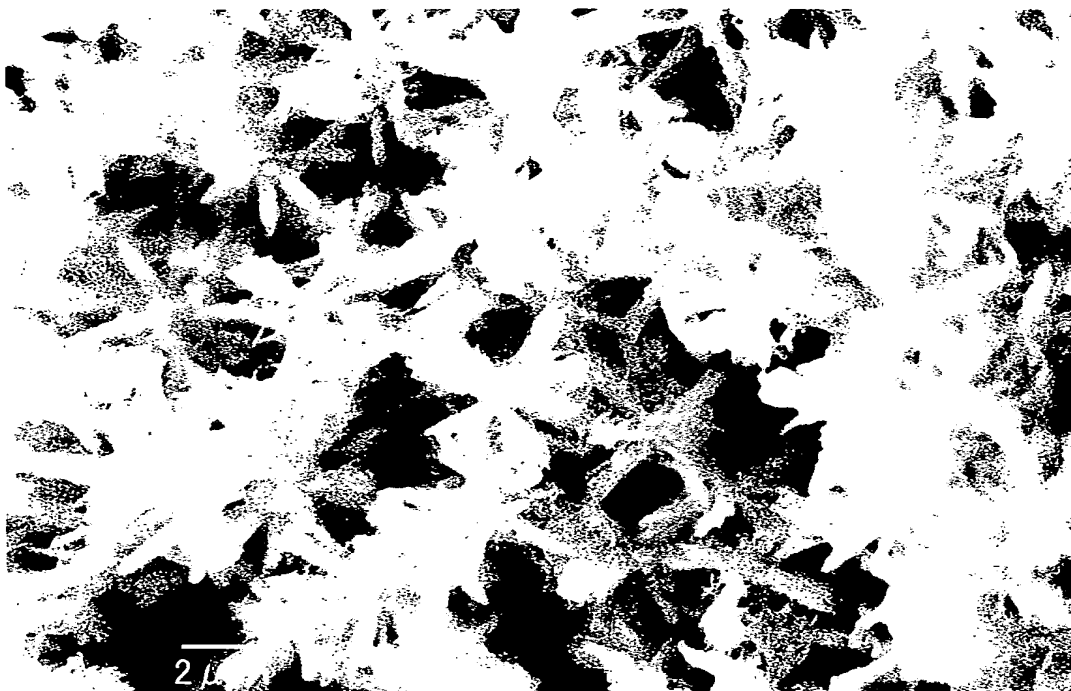


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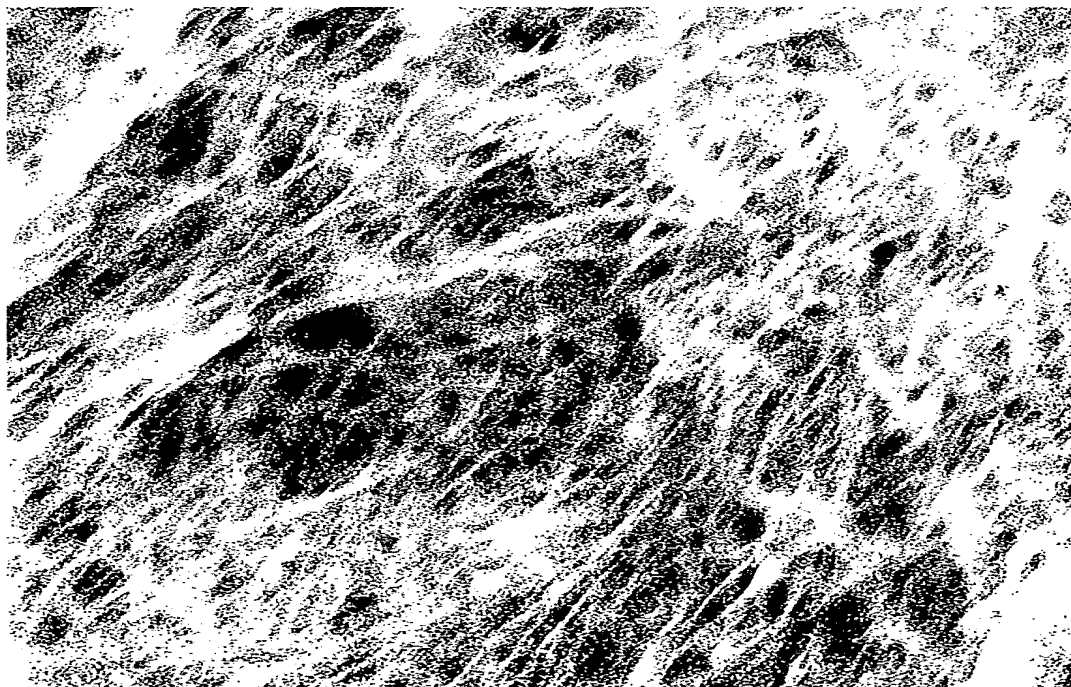
[Fig. 2]



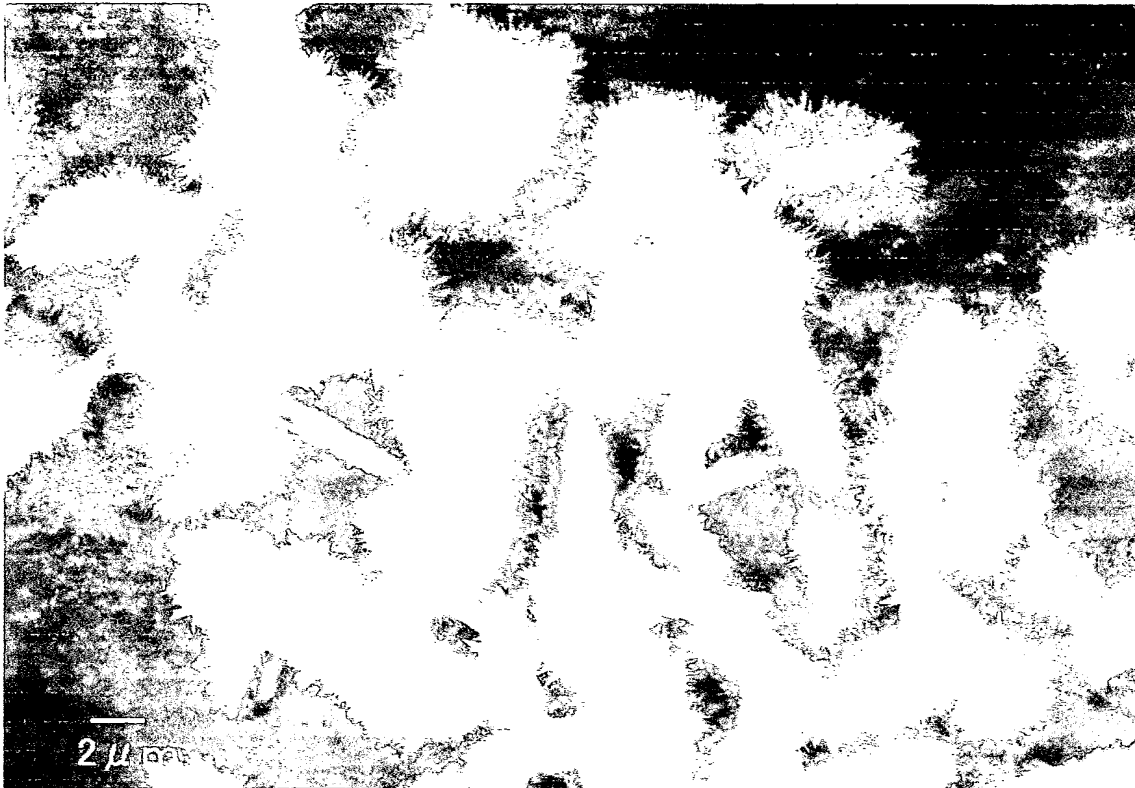
[Fig. 3]



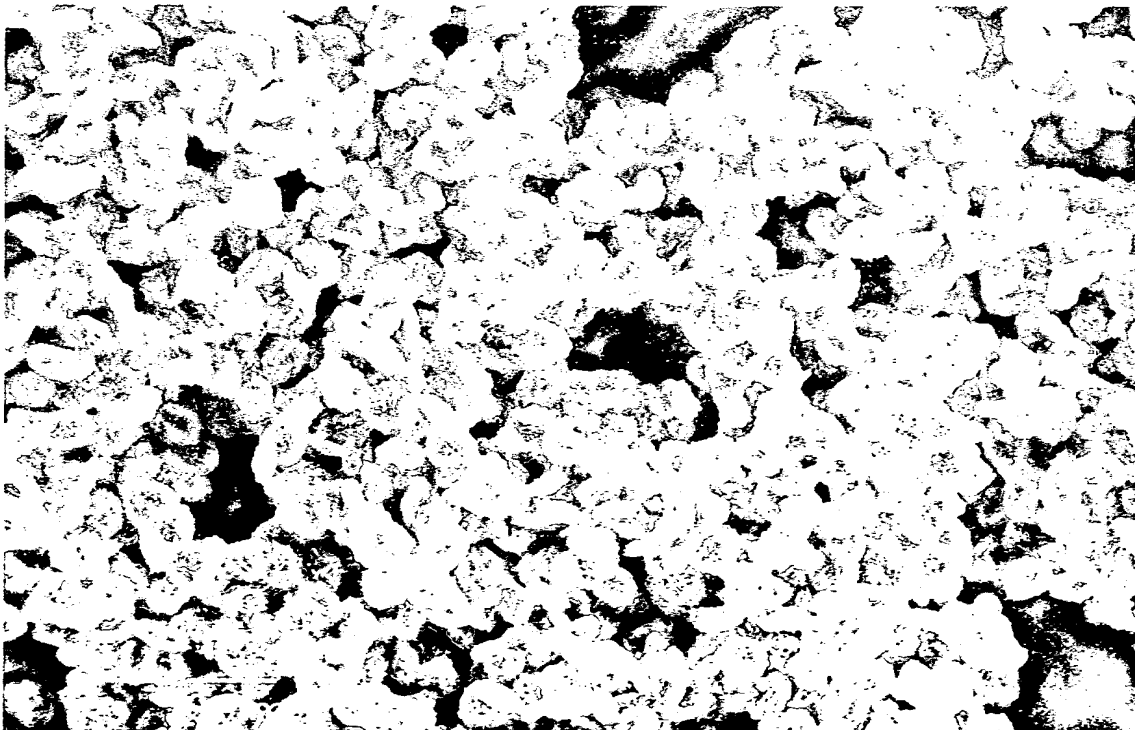
[Fig. 4]



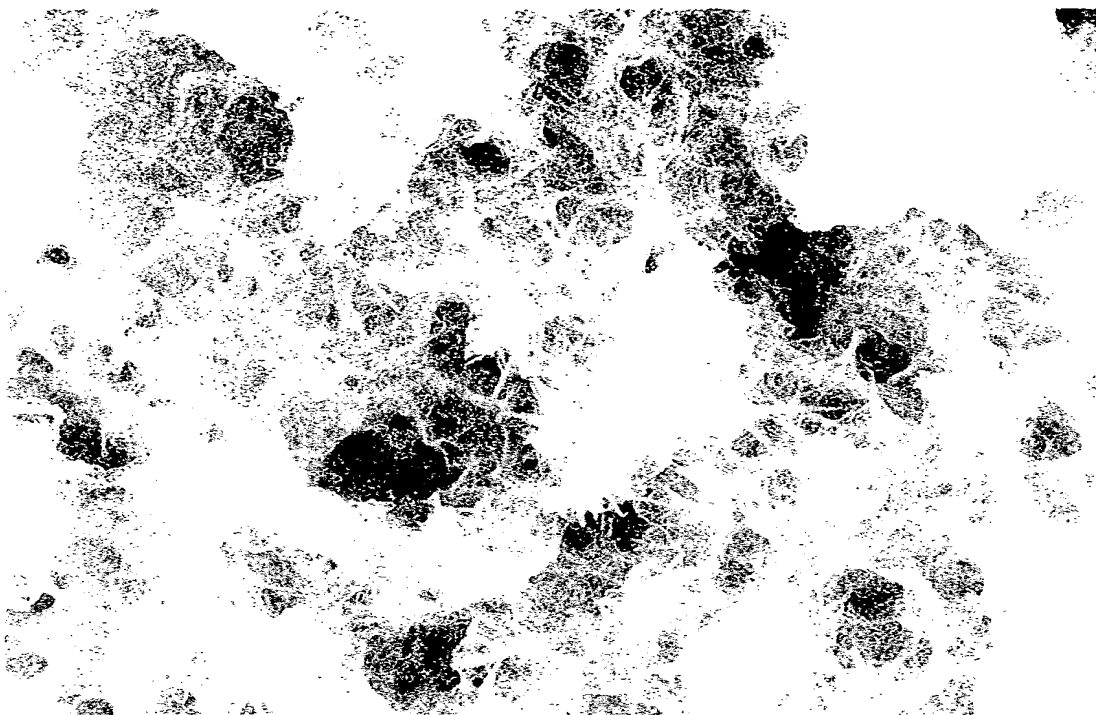
[Fig. 5]



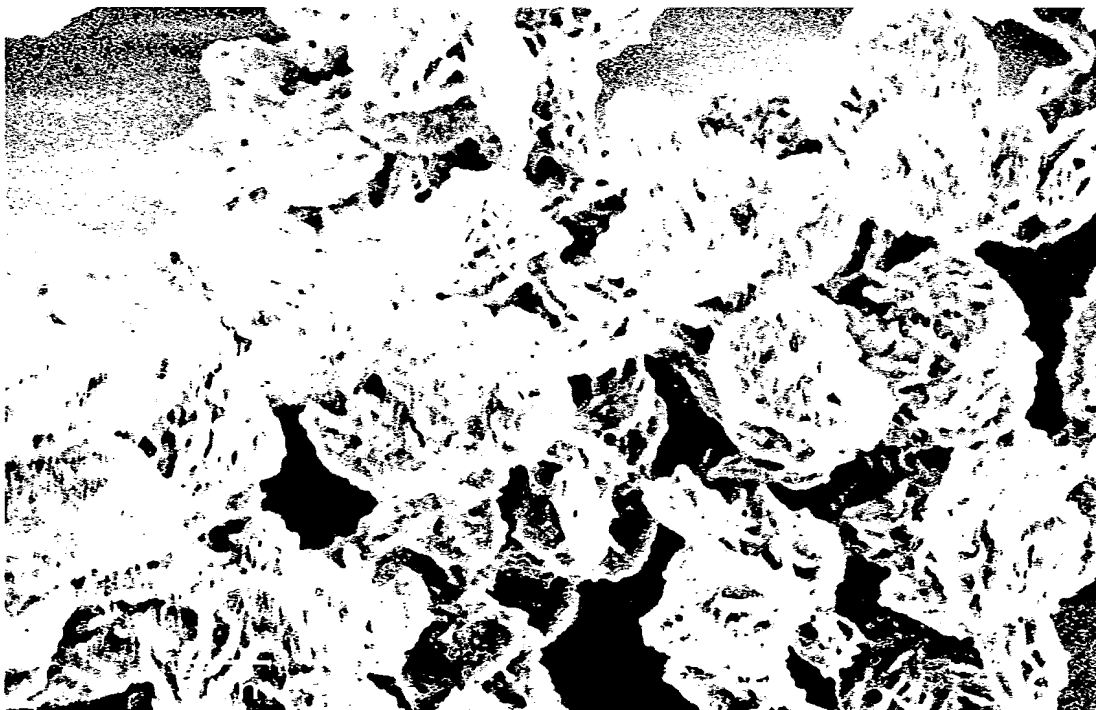
[FIG. 6]



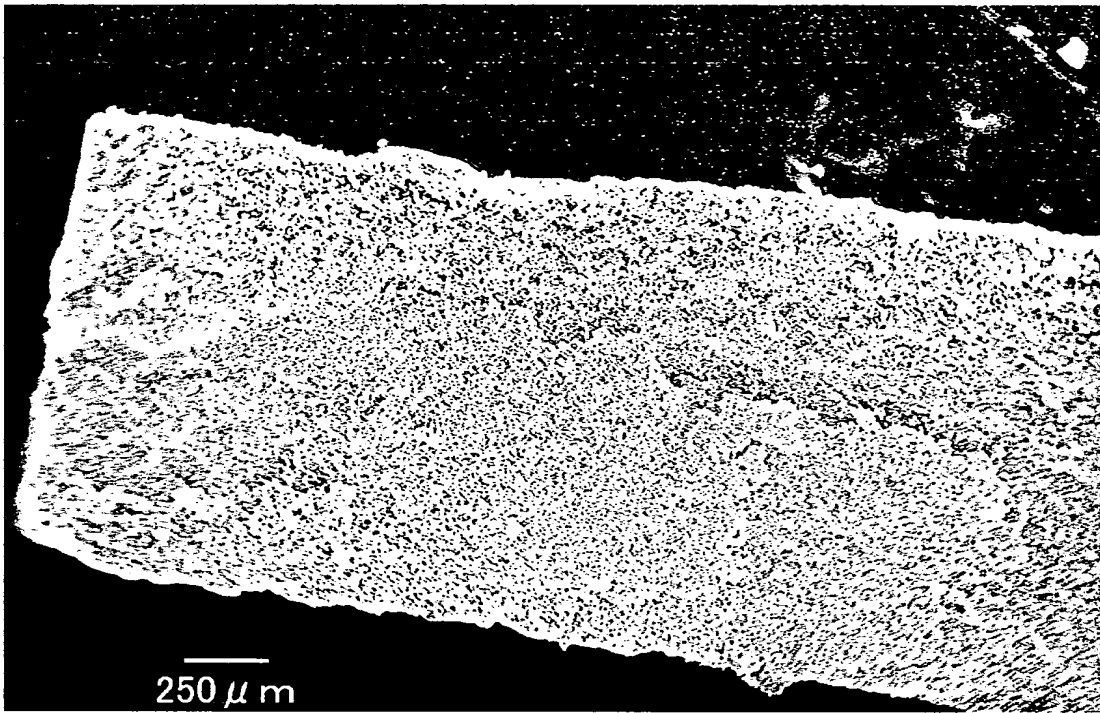
[Fig. 7]



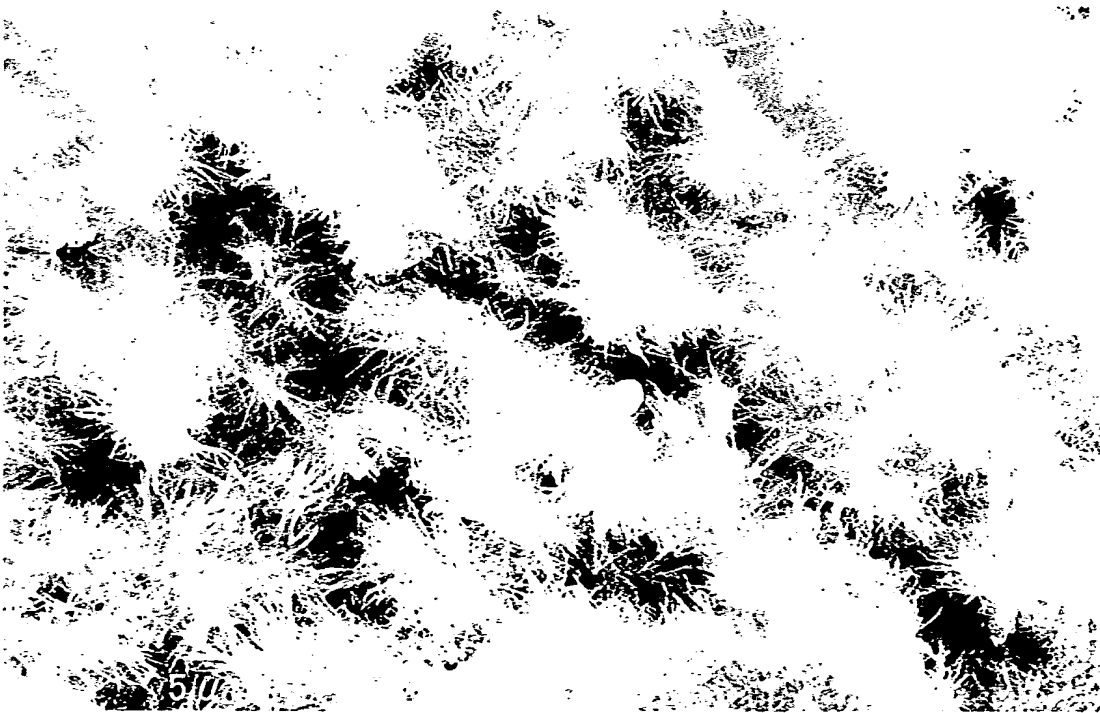
[Fig. 8]



[Fig. 9]



[Fig. 10]



[Document Name] ABSTRACT

[Abstract]

[Objective] To provide a hybrid between a polymer  
crystal controlled in various forms and a silica, and  
5 provide a simple method for producing a hybrid between a  
polymer crystal and a silica.

[Means for Achieving the Objective] In the present  
invention, a polymer crystal having a straight-chain  
polyethyleneimine skeleton can form various space forms.

10 The various space forms are copied to the silica, and  
thereby, the hybrids between the aforementioned polymer  
crystals and the silica have various complicated forms. In  
addition, the hybrids of the present invention can proceed a  
sol-gel reaction on the surface of the polymer crystal  
15 having the straight-chain polyethyleneimine skeleton.  
Thereby, a hybrid between the silica and the polymer crystal  
in which the surface of the crystal is covered with the  
silica can be easily obtained.

[Selected Drawing] Fig. 2